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 *              W E L C O M E   T O   T H E                     *
 *          U. S.   P A T E N T   T E X T   F I L E             *
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=> s 4940760/pn
L1            1 4940760/PN

=> s l1 and anion
          43035 ANION
L2            1 L1 AND ANION

=> d l2 hit
US PAT NO:      4,940,760 :IMAGE AVAILABLE:          L2: 1 of 1
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ABSTRACT:

Group Transfer Polymerization (GTP) process for preparing a "living" polymer, the process comprising contacting under polymerizing conditions in a polymerization medium, at least one acrylic or maleimide monomer with an initiator which is a tetracoordinate organosilicon, organotin or organogermanium compound having at least one GTP initiating site and a catalyst which is or is a source of an **anion** selected from the group consisting of bifluoride, fluoride, cyanide, azide or a selected oxyanion, or a selected Lewis acid or Lewis base, the process further characterized in that the initiator or the **anion** or Lewis acid catalyst is chemically attached (grafted) to a solid support that is insoluble in the polymerization medium.

SUMMARY:

BSUM(12)

G. Cainelli et al., Synthesis Communications, Nov. 723 (1975) disclose **anion** exchange resins which are useful as catalysts in many organic reactions. The resins contain quaternary ammonium cations chemically bonded to a macroreticular resin such as Amberlite IRA-904; counter anions include oxyanions such as carboxylate.

SUMMARY:

BSUM(36)

The invention provides a Group Transfer Polymerization (GTP) process for preparing a "living" polymer, the process comprising contacting under polymerizing conditions in a polymerization medium, at least one acrylic or maleimide monomer with an initiator which is a tetracoordinate organosilicon, organotin or organogermanium compound having at least one GTP initiating site and a catalyst which is, or is a source of, an **anion** selected from the group consisting of bifluoride, fluoride, cyanide, azide or a selected oxyanion, or a selected Lewis acid or Lewis base, the process further characterized in that either, but not both, the initiator or the **anion** or Lewis acid catalyst is chemically attached

(grafted) to a solid support that is insoluble in the polymerization medium. By "a solid support that is insoluble in the polymerization medium" is meant a solid support material from which no detectable amount, using commonly available analytical techniques, is dissolved by exhaustive extraction with the polymerization medium. The invention also provides: GTP "living" polymer grafted to the initiator support; GTP initiator that is chemically attached (grafted) to an insoluble support; and process for preparing such a GTP initiator.

DETDESC:

DETD(16)

Examples 4A and 26 illustrate the preparation of an insoluble supported GTP initiator, from crosslinked polystyrene wherein the suitable functional group is chloromethyl, by reaction with a bis(silyl ketene acetal) in the presence of a GTP **anion**- or Lewis acid-catalyst. A similar reaction occurs when the support material contains --CHO groups. Temperatures of about 0.degree. C to about 150.degree. C are suitable for these reactions. An insoluble supported GTP initiator can also be prepared directly from crosslinked polystyrene containing --RCN functions, such as cyanomethyl, by reaction with a soluble silyl, germyl or stannyl ketene acetal GTP initiator, or by low temperature silylation, germylation or stannylation via a lithium enolate using a lithium amide and chlorotrimethylsilane, chlorotrimethylgermane or chlorotrimethylstannane, as described in the preceding paragraph. If a chain transfer agent, such as described in U.S. Pat. No. 4,656,233, supra, is attached to the insoluble support material, then Group Transfer Polymerization of an acrylic monomer in the presence of such a chain transfer agent-containing support will produce a supported (grafted) polymer. Such a chain transfer agent can be prepared, for example, by reaction of chloromethylated crosslinked polystyrene with tetraethylammonium cyanide.

DETDESC:

DETD(26)

More specifically, the **anion** of the GTP catalyst is rendered insoluble in the reaction medium by its attachment to a counter ion (cation) which, in turn, is chemically attached to the insoluble support. The counter ion can be a quaternary ammonium, sulfonium, phosphonium, or arsonium ion. The support is preferably polymeric and completely insoluble in the polymerization medium. The insolubility is most commonly conferred by crosslinking. Catalytic activity is generally greater when crosslink density is low and the polymeric support is swelled by the liquid reaction medium.

DETDESC:

DETD(27)

Numerous polymeric supports are suitable for use in the invention process, such as polystyrenes, polyamides, polyesters, polyvinylpyridinium salts, polyethylene oxides, polyethers, acrylic polymers, polysulfones, polyolefins and polysulfides. The polymeric support must be insoluble in the polymerization medium, and this insolubility may be achieved by crosslinking, as indicated above. When used in conjunction with the catalyst, the polymeric support, if not inherently a polycation such as a polyvinylpyridinium salt, must be functionalized to provide a covalently bound cation to serve as the counter ion for the catalytic **anion**. Many methods for such functionalization of polymers have been described in the literature, for

example, Akelah and Sherrington, Chem. Rev., 81, 557 (1981); Manecke and Storck, Angew. Chem., Int. Ed. Engl., 17, 657 (1978); and Darling and Frechet, J. Org. Chem., 51, 2270 (1986). Technology for covalent functionalization of minerals with quaternary ammonium salts has been described by Arkles, Chemtech, 7, 766 (1977). Example 13 herein provides a special case where the catalyst is attached directly to the silicon atom of a supported silyl ketene acetal for use in polymerization of gaseous monomers.

DETDESC:

DETD(29)

The general conditions for carrying out the polymerizations using the insolubilized **anion** catalysts are the same as those for the homogeneous polymerizations described in the aforesaid patents and patent applications with respect to temperature, solvent, initiator, and monomer. The amount of insolubilized catalyst to be used depends on the amount of catalytic **anion** on the support (generally expressed as millequivalents per gram of polymer). The catalyst will generally be operable in the same concentration range as described for the homogeneous systems. If the support is nonswellable, higher concentrations of catalyst are desirable.

DETDESC:

DETD(34)

Experiment C-2 is similar to Experiment C-1, except that sodium acetate, rather than tetrabutylammonium acetate, was used for the **anion**-exchange. A potential advantage of the method of Experiment C 2 over that of Experiment C-1 is that, should any of the ion exchange reagent (sodium acetate or tetrabutylammonium acetate) remain with the resin after the washing processes, the sodium acetate would be virtually insoluble in the tetrahydrofuran (THF) used as the polymerization medium (in contrast to tetrabutylammonium acetate) and would be unlikely to produce GTP catalysis in solution.

DETDESC:

DETD(38)

Experiment C-6(A) demonstrates another preparation of a supported catalyst in which the **anion** (an aryl acetate) is bound covalently to the support. Thorough extraction and further washings in Experiment C-6(B) appear to have eliminated unbound base.

DETDESC:

DETD(69)

Comparative Experiment 1 demonstrates the preparation of a supported carboxylate in which the **anion** is covalently bound to the support and tetrabutylammonium is the counter ion.

DETDESC:

DETD(82)

The procedure of Experiment C-3 was followed using sodium acetate instead of sodium m-chlorobenzoate for the **anion**-exchange. Anal. found: N 0.84, Br 2.48% corresponding to 0.6 meq/g of N and 0.3 meq/g of Br. Thus, only about 50% of the bromide ion was exchanged for acetate

ion.

DETDESC:

DETD(152)

An 8 cm column of beads of "Amberlyst" A-27 macroreticular ion-exchange resin, a polystyrene heavily crosslinked with divinyl benzene and containing quaternary ammonium chloride terminal groups, was treated with a solution of 250 mL of sodium acetate in 300 mL of distilled water to convert the **anion** from chloride to acetate. The column was then washed with 500 mL of water to remove excess sodium acetate.

CLAIMS:

CLMS(1)

We claim:

1. Group Transfer Polymerization (GTP) process for preparing a "living" polymer, the process comprising contacting under polymerizing conditions in a polymerization medium, at least one acrylic or maleimide monomer with an initiator which is a tetracoordinate organosilicon, organotin or organogermanium compound having at least one GTP inititaing site and a catalyst which is, or is a source of, an **anion** selected from the group consisting of bifluoride, fluoride, cyanide, axide or a selected oxyanion, or a selected Lewis acid or Lewis base, the process further characterized in that the initiator is chemically attached to a solid support that is insoluble in the polymerization medium.